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㊹ **Method for cleaning metal parts.**

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Description

The present invention relates to a method for cleaning unbrazable metal parts sufficiently to render them brazable and more particularly, to a method for the low temperature cleaning of such parts with an atmosphere having the elements H-O-C-F so that the parts can be, thereafter, brazed or otherwise bonded.

Late model gas turbine engines for example, those on the Boeing 747, the DC-10, and the Lockheed 1011) employ in their turbine sections nickel based alloys that are gamma prime hardened. Many other engines contain such materials, and the use of gamma prime hardened alloys will no doubt increase in the future due to the desirable properties of these super-alloys.

The problem is that engine parts made of such alloys are very expensive and, at present, are not repairable when crack damaged due to metal fatigue. Attempts to weld repair such components result in post-weld cracking. Likewise, conventional brazing cannot be effected because nickel-base braze alloys will not run on the gamma prime hardened surfaces. Thus, although a molten brazing alloy under high vacuum might stick new gamma prime hardened parts together, it has not previously been possible to place brazing alloy inside cracks in damaged gamma prime hardened alloy parts.

A successful braze is manifest when braze material is placed at the source of a crack (say 0.001 inch wide (0.025 mm) and one-half inch (0.0127 mm) long) and, at brazing temperature, not only melts and sticks to the parent material, but also runs into and fills the length of the crack. Apparently, in use a gamma prime hardened alloy becomes oxidized (and/or sulfuridized) to the extent that the aluminum, titanium and chromium oxides (or sulfides) which coat the surface of the part, including the surfaces of the crack, prevent successful repair by brazing.

Accordingly, it has been recognised that such parts must be cleaned if they are to be brazed. One suggestion is to use chromium fluoride (CrF_3) and hydrogen (H_2) to clean damaged parts of gamma prime hardened alloys prior to a braze repair. It is speculated that the following reaction mechanism takes place:

1) $(CrF_3 3/2H_2/O) + H_2 \xrightarrow{\Delta} 3HF + Cr + H_2O + H_2$

2) $MO_x + HF \rightarrow MF_x + H_2O + M$
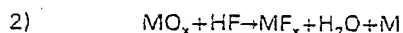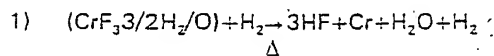
If, then, MF_x is volatile at the reaction temperature, the oxide is effectively reduced and the base metal (M) should be brazable. However, uniform reproducibility of results is for some reason lacking and many parts cleaned by this process are still not brazable.
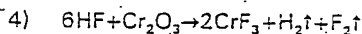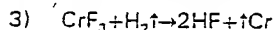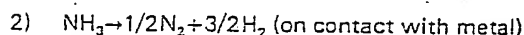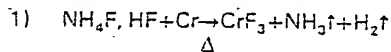
A much more effective process is not disclosed and claimed in our European Patent EP—A—0 003 660. European patent application No. 79300164.5.) However, that application is for the most part directed to cleaning crack-damaged gamma prime hardened alloys. It has now been established that a similar process is also effective to cleaning other metals, especially stainless steels, superalloys, and solid solution superalloys, as well as the gamma prime hardened nickel alloys. However, the temperature required by all prior cleaning processes is relatively high.

Fabrication of stainless steel composites by nickel brazing has long been of commercial interest. Before such devices can be fabricated by brazing, however, it is necessary to clean the faying surfaces of all metal oxides (or other compounds). The problem arises because the surfaces of such alloys are covered with a passive film which will not be wetted by a brazing alloy. The most stable oxide in such a film is that of chromium, and any pre-braze cleaning technique necessarily centres on this compound. It is necessary to reduce the chromium oxide (and all other oxides) to the metallic element before brazing can be accomplished.

A technique that is commonly employed to prepare such alloys for brazing is that of exposing them to a dry hydrogen atmosphere at high temperatures (>1000°C). Hydrogen cleaning is highly functional but has the disadvantage that the cleaning only takes place at temperatures that are near to or higher than the brazing temperature. Therefore, in situ cleaning and brazing of stainless steel and superalloy assemblies is often not practicable.

It is known that stainless steel can be brazed in a stable reducing atmosphere of fluoride. In a paper presented by the Toulouse, France, Microturbo Company representatives at the American Welding Society (AWS) meeting in Philadelphia in April 1977, entitled "Brazing Stainless Steel in a Stable Reducing Atmosphere of Fluoride," there is described a brazing process carried out in a halogen atmosphere obtained by the decomposition of fluorine salts such as ammonium bifluoride. acid and chromium fluoride. The proposed reactions are:

1) $NH_4F, HF + Cr \xrightarrow{\Delta} CrF_3 + NH_3\uparrow + H_2\uparrow$

2) $NH_3 \rightarrow 1/2N_2 + 3/2H_2$ (on contact with metal)

3) $CrF_3 + H_2\uparrow \rightarrow 2HF + \uparrow Cr$

4) $6HF + Cr_2O_3 \rightarrow 2CrF_3 + H_2\uparrow + F_2\uparrow$

There are two pertinent observations regarding these reaction: a) the object would appear to be the production of HF gas which, in turn, does the cleaning, and b) any elemental fluorine that forms is produced downstream of the work piece (see reaction 4). It is noted that in the presented paper there is an indication that "the

technique cannot be used on assemblies of materials having a high level of electropositivity, such as titanium and zirconium, "and" it is essential to avoid the introduction of carbon into the furnace during brazing".

Similarly, Moore in U.S. Patent No. 3,585,819, discloses a process of fluxing metal parts with a stable, non-oxidizing atmosphere containing HF gas. The metal parts are ones such as steels which are to be brazed or soldered.

Finally, reference is made to Low U.S. Patent No. 2,851,387. This relates to a process for nitriding high chromium stainless steels. In Low's discussion of the prior art he notes that all prior processes of depassifying such steels require immediate nitriding or the internal effects of the depassifying were lost. A specific purpose of his invention is a combined activating and nitriding operation which avoids any problems of interruption in the sequence of steps. The combined operations are provided by a mixture of decomposed fluorocarbon resin gases and ammonia gas. The result is a nitrided product, but it is believed that a cleaned, brazable product would not be produced.

Accordingly, the need still exists for a relatively low temperature method for cleaning metal parts to render them brazable or otherwise bondable. That need is met by the present invention which utilizes a simple, inexpensive method for cleaning metal parts, including stainless steels, superalloys, solid solution superalloys, as well as gamma prime hardened nickel alloys at relatively low temperature.

The present invention consists in a method for cleaning a surface of an unbrazable metal part so as to render it brazable or otherwise suitable for metal to metal bonding by subjecting said part in a hermetically sealed chamber to an atmosphere containing the elements C-H-O-F at a temperature at which reaction occurs, said method being characterized in that said part is heated in an atmosphere in which oxygen is present in moisture which is present as a trace impurity, the atomic ratio of H/O therein is 10^4 or greater, and said temperature does not exceed 850°C and is, preferably, 700—850°C. The part being treated is allowed to remain in the chamber in this atmosphere for a period of time sufficient to clean the part and render it brazable and it is then cooled prior to removing it from the chamber.

It has been found that a key to this relatively low temperature cleaning operation is control of the H/O atomic ratio in the C-O-H-F gaseous atmosphere containing moisture as an impurity. When using such a gaseous atmosphere under controlled conditions, it is possible adequately to clean the metal parts at temperatures below 850°C. This is to be compared with a commonly employed method of preparing metal parts for brazing by exposing them to a dry hydrogen atmosphere at temperatures above 1000°C. The energy savings obtained from relatively low temperature cleaning are apparent, as is the ability to perform in situ cleaning and brazing. At an H/O atomic ratio of 10^4 or greater, the metal parts can be adequately cleaned at temperatures as low as approximately 800—850°C. At an H/O atomic ratio of around 10^5, the metal parts can be adequately cleaned at temperatures as low as approximately 700—750°C. At even greater H/O atomic ratios, even lower cleaning temperatures are possible.

However, much higher H/O atomic ratios are difficult to obtain. The H/O atomic ratios of 10^4 and 10^5 correspond to approximately 200 and 20 ppm H_2O, respectively, present as moisture constituting an impurity in the hydrogen gas used as a component of the C-O-H-F atmosphere. It is difficult to obtain hydrogen gases which are less moist and which have fewer parts per million of moisture present as an impurity.

That is, the oxygen in the C-O-H-F system of the present invention comes from moisture present as an impurity in the other components. The hydrogen gas is the main source of that moisture since it is possible otherwise to minimise its presence by deriving the carbon and fluorine component from thermally decomposed fluorocarbon resins. Addition of other oxidizing gases or, for that matter, any substantial amounts of other non-inert gases of any type is to be avoided.

Polytetrafluoroethylene resin liberates fluorine when heated to 350°C or higher and the rate of evolution sharply increases between 400° and 450°C. The liberation of fluorine is only a part of the decomposition process and other gases evolved by the thermal decomposition are also important in the low-temperature cleaning process of the present invention.

Actually, the number of organic gases that could form in the system used in the present invention is so large that it defies complete analysis. Thus a simplification must be adopted. When reduced to its simplest yet feasible form, the system would contain only fluorocarbons containing only carbon and fluorine and then only the two most simple of these one of which involves a carbon to carbon double bond, namely, tetrafluoroethylene (C_2F_4) and the other is tetrafluoromethane (CF_4). It is believed that C_2F_4, when mixed with moist hydrogen, reduces the water content by the reaction:

$$C_2F_4 + 2H_2O \rightarrow 4HF + 2CO$$
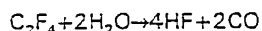
Thus, the decomposed fluorocarbon resin gases are not only moisture-free, but also react with the moisture otherwise introduced to, overall, create an extremely reducing atmosphere. That atmosphere is capable of cleaning metal surfaces of formed oxides to render them brazable or otherwise bondable.

As mentioned, in many such applications, the

most thermodynamically stable oxide that is found in the oxidation or passivation layer is that of chromium. Such layers may be a disadvantage in welding and/or a deterrent to brazing. Furthermore, due to the relative stability of its oxide, if Cr could be stabilised in favour of its oxide, the other metallic elements in the oxide film should be similarly reduced. Thus, if an oxidised alloy which contains chromium were exposed to an atmosphere in which elemental chromium is stable, and then cooled in an atmosphere which had insufficient oxidising power to reform the oxides, the result is an alloy at room temperature which is readily brazable. This is accomplished by the present cleaning process.

As mentioned, a preferred embodiment of the present invention is to utilise a thermally decomposable fluorocarbon resin together with hydrogen gas containing moisture as a trace impurity to clean unbrazable metal parts and render them brazable at commercial vacuum levels, 133.322×10^{-2} to 10^{-4} Pa (10^{-2} to 10^{-4} Torr).

In terms of the ability to clean at relatively low temperature, it is now known that this is dependent upon the H/O atomic ratio found in the C-O-H-F atmosphere containing moisture as a trace impurity. Using a H/O atomic ratio of 10^5, a pressure of 98066.5 Pa (1 atms.), and considering only the chromium portion of a stainless steel or solid solution superalloy, it appears that at some temperature before the system reaches 700°C and up to 800°C, the Cr_2O_3 in the oxidation layer will tend to convert to CrF_3. At 800°C the CrF_3 and any remaining Cr_2O_3 will tend to convert to elemental Cr. The system can be held at below 850°C at a designated point P (discussed below) until all Cr compounds have been converted to Cr metal. At this point, the system should be cooled under pure H_2 or a dry inert gas. The result will be an oxide (and fluoride) free metal surface with a thin layer of chromium metal.

The point P corresponds to the C/H, F/H and H/O atomic ratios as follows:

C/H=0.004
F/H=0.04
H/O=10^5

The foregoing conditions result in the following equations:

$$\frac{P_{CF_4}}{2P_{H_2}+2P_{H_2O}+P_{HF}}=0.004$$

$$\frac{4P_{CF_4}+P_{HF}}{2P_{H_2}+2P_{H_2O}+P_{HF}}=0.04$$

$$\frac{2P_{H_2}+2P_{H_2O}+P_{HF}}{P_{H_2O}}=10^5$$

$$P_{H_2}+P_{H_2O}+P_{CF_4}+P_{HF}=1.0$$

These equations indicate a gas mixture of the following approximate composition:

H_2=94.5 v/o
HF=4.7 v/o
CF_4=0.8 v/o
H_2O=0.002 v/o

The gas is readily contrived by creating a mixture of HF, CF_4, and H_2 (with 20 ppm of H_2O) in the proper proportions. The preferred source of those gases is thermally decomposed fluorocarbon resin and low mositure containing H_2 gas. Other sources may also be used as long as the proportions necessary to obtain the calculated P points are present. This gas mixture will stabilize chromium in preference to its oxide or fluoride under the conditions that thermodynamic equilibrium is reached.

Since the chromium oxides are the most difficult to destabilize, it should be apparent that by doing so, the present invention enables the low temperature cleaning of metal parts, including stainless steel, superalloys, solid solution superalloys, as well as gamma prime hardened nickel based alloys, by removing chromium oxides and any less stable oxides. It also enables the in situ brazing of those parts at such low temperatures.

Claims

1. A method for cleaning a surface of an unbrazable metal part so as to render it brazable or otherwise suitable for metal to metal bonding by subjecting said part in a hermetically sealed chamber to an atmosphere containing the elements C-H-O-F at a temperature at which reaction occurs, said method being characterized in that said part is heated in an atmosphere in which oxygen is present in moisture which is present as a trace impurity, the atomic ratio of H/O therein is 10^4 or greater, and said temperature does not exceed 850°C and is, preferably, 700—850°C.

2. A method as claimed in claim 1, further characterized in that said H/O atomic ratio is substantially 10^4 and said temperature is 800—850°C.

3. A method as claimed in claim 1, further characterized in that said H/O atomic ratio is substantially 10^5 and said temperature is 700—750°C.

4. A method as claimed in any of the preceding claims, further characterized in that said atmosphere is produced by the thermal decomposition of a fluorocarbon resin, preferably polytetrafluoroethylene, in the presence of added hydrogen gas containing less than 200 ppm of moisture as a trace impurity.

Patentansprüche

1. Verfahren zur Reinigung der Oberfläche

eines nicht hartlötbaren Metallgegenstandes derart, daß er hartlötbar oder einer anderen Metall-zu-Metall-Bindung zugänglich wird, bei welchem der Gegenstand in einer hermetisch abgeschlossenen Kammer einer die Elemente C-H-O-F enthaltenden Atmosphäre bei einer Temperatur, bei der Reaktion eintritt, ausgesetzt wird, dadurch gekennzeichnet, daß der Gegenstand in einer Atmosphäre erhitzt wird, in der Sauerstoff als Feuchtigkeit vorhanden ist, die als Spuren-Verunreinigung vorhanden ist, wobei das Atom-Verhältnis H/O darin gleich oder größer als 10^4 ist, und daß die Temperatur 850°C nicht überschreitet und vorzugsweise 700—850°C beträgt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das H/O-Atom-Verhältnis im wesentlichen 10^4 und die Temperatur 800—850°C beträgt.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das H/O-Atom-Verhältnis im wesentlichen 10^5 und die Temperatur 700—750°C beträgt.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Atmosphäre durch thermische Zersetzung eines Fluorkarbonharzes, vorzugsweise von Polytetrafluoräthylen, in Gegenwart von hinzugefügtem Wasserstoffgas, das weniger als 200 ppm Feuchtigkeit als Spuren-Verunreinigung enthält, erzeugt wird.

Revendications

1. Procédé pour le nettoyage de la surface d'une pièce métallique non-brasable de façon à la rendre brasable ou autrement adaptée à un collage métal sur métal, en soumettant cette pièce, dans une chambre hermétiquement fermée, à une atmosphère contenant les éléments C-H-O-F à une température à laquelle se produit la réaction, procédé caractérisé en ce que la pièce est chauffée dans une atmosphère dans laquelle l'oxygène est présent dans l'humidité présente sous forme de traces, le rapport atomique H/O y étant supérieur ou égal à 10^4, la température ne dépassant pas 850°C et étant de préférence comprise entre 700 et 850°C.

2. Procédé selon la revendication 1, caractérisé en ce que le rapport atomique H/O est essentiellement égal à 10^4 et que la température est comprise entre 800 et 850°C.

3. Procédé selon la revendication 1, caractérisé en ce que le rapport atomique H/O est essentiellement de 10^5 et que la température est comprise entre 700 et 750°C.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que l'atmosphère est produite par la décomposition thermique d'une résine fluorocarbonée, de préférence le polytétrafluoréthylène, en présence d'hydrogène gazeux ajouté contenant moins de 200 ppm d'humidité sous forme de traces.

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